Chemotherapy of Smut and Rust Pathogens in Poa pratensis by Thiazole Compounds

John R. Hardison

Research Plant Pathologist, Plant Science Research Division, ARS, USDA, and Department of Botany and Plant Pathology, Oregor Agricultural Experiment Station, Corvallis 97331.

Cooperative investigations of the Plant Science Research Division and the Oregon Agricultural Experiment Station. Published with approval of the Director as Technical Paper No. 3022, Oregon Agricultural Experiment Station.

Mention of a trademark, code name, or proprietary product is for identification purposes, and does not constitute a guarantee or warranty of the product by the USDA, nor does it imply its approval to the exclusion of other products that may also be suitable.

Acknowledgment is made to the UniRoyal Corporation for supplies of the experimental chemicals and technical advice. Appreciation is expressed to the UniRoyal Corporation, to the Penncross Bentgrass Growers Association, and to the Merion Bluegrass Association for support of this research through Oregon State University.

Accepted for publication 2 July 1971.

ABSTRACT

Five proprietary thiazole compounds were evaluated for systemic fungicidal properties against *Ustilago striiformis* (stripe smut), *Urocystis agropyri* (flag smut), and *Puccinia striiformis* (stripe rust) after soil application and root uptake in diseased *Poa pratensis* 'Merion'. The parent thiazole compound, 2,4-Dimethyl-5-carboxanilido-thiazole, eradicated *U. striiformis* and *U. agropyri*, and gave good control of *P. striiformis*. A 2-amino substitution on the parent thiazole heterocycle increased activity against both smuts and maintained good rust control. A 2-methyl substitution on the phenyl ring with an unaltered thiazole failed to control stripe smut, but maintained good control of flag smut and rust. A 2-amino substitution on the thiazole heterocycle plus either a 3-methyl or a 3-methoxy substitution on the phenyl ring seriously impaired activity against all three diseases, although phytotoxicity was reduced. The parent compound and the 2-amino substitution analogue were more active against *U. striiformis* and more phytotoxic than a related oxathiin compound, oxycarboxin. The thiazole compounds were inferior to oxycarboxin for control of flag smut and stripe rust. Phytopathology 61: 1396-1399.

Additional key words: chemotherapy, Merion Kentucky bluegrass.

Systemic fungicides are attractive candidates for chemical control of stripe rust, *Puccinia striiformis*, stripe smut, *Ustilago striiformis*, and flag smut, *Urocystis agropyri*, in grasses (2,3,4). The systemic fungicide, 2,4-Dimethyl-5-carboxanilido-thiazole (G696) and its 2-amino substitution analogue, 2-Amino-4-methyl-5-carboxanilido-thiazole (F849), have fungicidal properties similar to the systemic fungicides, carboxin and its sulfone form, oxycarboxin. Control of loose smuts in wheat and barley and other head or kernel smuts in cereals by these four systemic chemicals applied to seeds is well documented, as reviewed by Snel et al. (5).

In foliar sprays on bean, G696 was slightly less active than oxycarboxin and carboxin against *Uromyces phaseoli* var. *typica* (5). In the same tests, F849 was slightly more active than G696 and oxycarboxin, but slightly less active than carboxin (5). Against *Ustilago maydis*, F849 in in vitro tests was more active than G696 but less active than carboxin, but both G696 and F849 were much more active than oxycarboxin (5).

Urocystis agropyri and *Ustilago striiformis* were eradicated by G696 in diseased plants of *Poa pratensis* 'Merion' in several greenhouse tests in Oregon in earlier studies. Drenching bluegrass sod with G696 resulted in partial control of *U. striiformis* in Wisconsin (6) and in New Jersey (1).

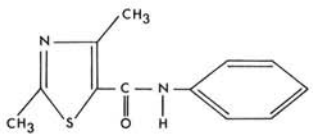
Although G696 will eradicate both *U. agropyri* and *U. striiformis* in *P. pratensis*, the dosages necessary are excessive for field application and are phytotoxic. The objective of the present study was to evaluate additional thiazole derivatives for improved effectiveness in comparison with G696 and a standard oxathiin compound, oxycarboxin, in a continuing search for more effective fungicides.

MATERIALS AND METHODS.–Tests were conducted in a greenhouse with small plants of *Poa pratensis* L. 'Merion' infected with either *Ustilago striiformis* (Westend.) Niessl or *Urocystis agropyri* (Preuss) Schroet. A supply of plants infected with the smuts was maintained by clonal propagation of diseased field plants with smut in every shoot. Plant material was separated into small plants, each with four to six shoots, and transplanted to 150 ml of sandy loam soil, pH 5.8, in plastic cups or in 600 ml of soil in 4-inch-sq plastic pots, each with four drainage holes. After good root development (4 to 8 weeks), and just before treatment, the plants and soil were transferred to cups or pots without drainage holes to prevent loss of chemical. For tests with *Puccinia striiformis* West., healthy plants of Merion Kentucky bluegrass were propagated in the same fashion. The test plants were dusted with abundant urediospores 7 days after application of chemicals to soil, and held in a moist chamber for 12 hr on each of three successive nights.

Results with *U. striiformis* and *U. agropyri* were measured by appearance of smut-free leaf tissue in treated plants compared with untreated plants in three replications. Control of *P. striiformis* was evaluated at 14 and 28 days after inoculation by

noting the presence or absence and type of rust infections.

The basic thiazole molecule, G696, contains a 2,4-dimethyl thiazole heterocycle joined at the 5-carbon to a carboxanilide moiety, and substitutions on either or both of these moieties creates the several analogues. The structure of the basic molecule (G696) is as follows:



The basic heterocycle is modified by substitution of an amino radical at the 2-carbon in compounds F849, G593, and H111. Substitutions on the phenyl ring include: 2-methyl (H115), 3-methyl G593), and 3-methoxy (H111). The identities for these analogues are: 2-Amino-4-methyl-5-*N*-(3-methylphenyl)-carboxamido-thiazole (G593), 2-Amino-4-methyl-5-*N*-(3-methoxyphenyl)-carboxamido-thiazole (H111), and 2,4-Dimethyl-5-*N*-(2-methylphenyl)-carboxamido-thiazole (H115).

Wettable powder formulations of G696 and F849 were tested. The other derivatives were tested as technical grade material, and were dissolved in acetone, mixed with small quantities of surfactant, Tween 20 (polyoxyethylene sorbitan monolaurate), and dispersed in water. Desired quantities of the suspended chemicals were placed in holes 2 cm deep in the soil at four locations surrounding each plant. All dosages are expressed as actual chemical.

Oxycarboxin was included in these trials for comparison, because its related structure contains an identical carboxanilide moiety joined instead to a 1,4-oxathiin heterocycle, and because it has shown strong activity against the three pathogens (4).

RESULTS.—*Ustilago striiformis*.—The parent compound, G696, has shown strong activity after soil application and root uptake in *P. pratensis* in many different tests beginning in February 1967. Eradication of *U. striiformis* was shown by absence of the pathogen for more than 1 year after application of the chemical.

Because of limited quantities of the analogues, tests of thiazole derivatives in comparison with G696 and oxycarboxin were made in small plastic cups containing 150 ml soil. The results show that a 2-amino substitution on the thiazole heterocycle (F849) increased activity against *U. striiformis*, but F849 increased phytotoxicity. In earlier tests, nearly complete loss of activity against *U. striiformis* resulted from a 2-amino substitution on the heterocycle plus a 3-methyl substitution on the phenyl ring (G593). Similarly, a 2-amino substitution on the thiazole ring plus a 3-methoxy substitution on the phenyl ring (H111) resulted in much less activity than the parent molecule. An unchanged thiazole moiety with a 2-methyl substitution on the phenyl ring (H115) severely reduced activity against stripe smut and greatly increased plant injury. In separate tests, small plants did not survive rates above 5 mg/150 ml soil.

In comparison with the other thiazole derivatives and with oxycarboxin, G696 and F849 have shown stronger activity against *U. striiformis*, but G696 and F849 caused more plant injury than oxycarboxin as

TABLE 1. Eradication of *Ustilago striiformis* in *Poa pratensis* 'Merion' by systemic fungicides applied to soil in the root zone

Chemical[a]	mg/150[b] ml soil	Weeks after application of chemical					
		0	4	6	8	12	16
		smutted shoots/total shoots in three pots					
G696	5.0	18/18	18/18	17/17	14/16	13/18	22/22
	10.0	18/18	19/20	15/18	1/11	0/23	1/30
	15.0	18/18	17/17	15/15	2/12	0/4	0/8
	20.0	16/16	16/17	15/18	0/11	0/18	0/21
F461	10.0	18/18	5/16	10/24	8/34	37/60	69/73
	15.0	16/16	0/13	0/19	0/33	15/53	56/76
	20.0	20/20	2/12	0/19	0/21	0/29	1/48
F849	5.0	17/17	15/15	14/16	13/16	15/36	29/42
	7.5	17/17	15/15	15/15	4/11	14/18	21/21
	10.0	16/16	16/16	17/17	[b]/15	2/17	5/7
	15.0	16/16	14/14	14/14	[b]/13	0/6	0/8
	20.0	20/20	20/20	18/18	[b]/16	0/7	1/14
H115	1.0	19/19	25/25	30/30	22/40	51/53	55/61
	2.5	20/20	28/28	31/31	38/39	50/50	61/61
	5.0	19/19	21/21	22/22	42/54	73/73	78/78
None		18/18	24/24	32/32	39/39	56/56	64/64

[a] G696 = 2,4-Dimethyl-5-carboxanilido-thiazole; F461 = 5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4,4-dioxide; F849 = 2-Amino-4-methyl-5 carboxanilido-thiazole; H115 = 2,4-Dimethyl-5-*N*-(2-methylphenyl)carboxamide-thiazole.

[b] Lack of growth prevented smut rating.

TABLE 2. Eradication of *Urocystis agropyri* in *Poa pratensis* 'Merion' by systemic fungicides applied to soil around infected plants

Chemical[a]	mg/150 ml soil	Weeks after application of chemical					
		0	4	6	8	12	16
		smutted shoots/total shoots in three pots					
G696	2.5	19/19	0/27	0/33	1/50	9/65	14/70
	5	20/20	0/19	0/26	0/36	0/48	0/47
	7.5	20/20	0/20	0/16	0/33	0/36	0/42
	10	19/19	2/16	0/17	0/29	0/33	0/36
F461	1	21/21	5/41	19/68	23/98	104/134	109/139
	2.5	18/18	0/27	0/39	0/63	0/72	0/78
	5	18/18	0/22	0/30	0/40	0/46	0/51
	7.5	20/20	0/24	0/26	0/49	0/54	0/54
	10	15/15	0/17	0/17	0/16	0/50	0/51
F849	2.5	21/21	6/35	3/39	11/64	37/77	47/78
	5	19/19	1/25	0/31	1/31	2/52	3/62
	7.5	20/20	2/17	0/14	0/26	0/34	0/36
	10	20/20	2/19	0/16	0/23	0/39	0/45
	15	21/21	3/17	0/10	0/26	0/31	0/34
	20	18/18	0/6	0/7	0/15	0/16	0/22
H115	1	18/18	7/28	9/52	16/73	63/95	38/120
	2.5	18/18	1/30	0/35	0/43	1/55	4/68
	5	21/21	2/25	0/28	0/41	0/54	0/68
None		17/17	28/28	44/44	60/60	73/73	79/79

[a] G696 = 2,4-Dimethyl-5-carboxanilido-thiazole; F461 = 5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4, 4-dioxide; F849 = 2-Amino-4-methyl-5-carboxanilido-thiazole; H115 = 2,4-Dimethyl-5-*N*-(2-methylphenyl)carboxamide-thiazole.

shown by the number of surviving shoots 16 weeks after chemical treatment (Table 1).

Urocystis agropyri.—In many separate tests, the parent compound, G696, controlled *U. agropyri* in *P. pratensis* 'Merion' after application of the chemical to soil. Eradication of *U. agropyri* was indicated in several tests by the absence of flag smut in previously diseased plants that were observed for more than 1 year after application of G696. In parallel small-scale tests, G696 has been more active than most other thiazole derivatives, but slightly less effective than the oxathiin standard, oxycarboxin (Table 2). The 2-amino substitution on the heterocycle (F849) slightly reduced the activity of the parent compound against *U. agropyri* (Table 2), but in other tests, F849 showed activity about equal to G696. In an earlier test, the 2-amino substitution on the thiazole heterocycle with substitution on the phenyl moiety of either a methyl at the 3-carbon (G593) or a methoxy at the 3-carbon (H111) resulted in complete loss of activity or in badly impaired control, respectively. A 2-methyl substitution on the phenyl ring with an unaltered thiazole heterocycle (H115) maintained good activity with eradication of *U. agropyri*, although effective dosages are close to the threshold of increased and severe plant injury. Compared to oxycarboxin, G696, F849, and H115 demonstrated strong activity against *U. agropyri*, although phytotoxicity is temporarily troublesome with all the compounds.

Puccinia striiformis.—When applied to 150 ml soil holding small plants of *P. pratensis* 'Merion' (each with five shoots) 7 to 10 days before inoculation, G696 restricted infection at 0.5 mg and prevented infection at 1 mg. The 2-amino substitution on the thiazole ring with unaltered phenyl (F849) gave nearly complete rust control at 1 mg that was superior to most other thiazole analogues, and about equal to G696.

The other analogues with a 2-amino substitution on the thizaole ring, G593 (with a 3-methyl substitution on the phenyl ring) and H111 (with a 3-methoxy substitution on the phenyl), were much inferior for stripe rust control compared to the parent compound, and were weakly active only at high dosages. The unaltered heterocycle with a 2-methyl substitution on the phenyl ring (H115) reduced infection at 1 mg and provided complete control at 2.5 mg/150 ml of soil. In comparison, oxycarboxin gave complete control at 1 mg and nearly complete control at 0.5 mg, about the same as for G 696.

Comparable results were obtained with G696 and oxycarboxin applied to 600 ml of soil holding larger plants with 15 to 20 shoots. F849 is a promising analogue for stripe rust control, but the other thiazole analogues gave inferior rust control as compared with G696, F849, and oxycarboxin. Although F849 and G696 may be promising candidates for rust control by root uptake in *P. pratensis*, the control is no better than that obtained by oxycarboxin.

DISCUSSION.—The in vivo evaluations indicate that the parent or basic molecule, G696, has the widest spectrum of activity and provides the most consistent control of all three diseases among the five thiazole derivatives studied. G696 eradicated *U.*

agropyri and *U. striiformis* in several separate trials, and treated plants have remained smut-free for extended periods. Similarly, G696 controlled stripe rust in repeated trials at dosages lower than other thiazole derivatives.

Compared to the parent, the 2-amino substitution on the heterocycle with an unaltered phenyl ring (F849) quenched activity against *U. striiformis*, increased activity against *U. agropyri*, maintained good activity against *P. striiformis*, and increased phytotoxicity. The 2-methyl substitution on the phenyl ring with unchanged heterocycle (H115) maintained activity against *U. agropyri*, seriously reduced activity against *U. striiformis*, maintained fairly good rust control, but greatly increased phytotoxicity. A 2-amino substitution on the heterocycle, combined with either a 3-methyl (G593) or a 3-methoxy (H111) substitution on the phenyl ring, resulted in loss of virtually all activity against the three pathogens, although these molecular changes reduced phytotoxicity.

Several of the thiazole derivatives compare favorably with oxycarboxin, which represents nearly the best of the oxathiin fungicides against these diseases. Oxycarboxin, G696, and F849 are about equal in systemic activity against all three diseases. Although H115 may be promising for control of *U. agropyri*, effective dosages are near the threshold of severe phytotoxicity. F849 may be promising for stripe rust control.

The thiazole compounds in the present paper have a carboxanilide moiety identical to that in the 1,4-oxathiin fungicides. Oxidation of the sulfur (S) in the oxathiin heterocycle (oxycarboxin) greatly increased systemic fungicidal activity over the nonoxidized form (carboxin) against *U. striiformis* and *U. agropyri* (4); therefore, thiazole analogues with an oxidized S in the heterocycle would be interesting candidates for tests of fungicidal activity against these pathogens. A 2,3-dimethyl substitution on the phenyl moiety should be considered, because this molecular modification increased activity in the oxathiin fungicides (4). A combination of a thiazole dioxide with a 2-methyl or a 2,3-dimethyl substitution on the phenyl ring with or without the 2-amino substitution on the heterocycle would also be interesting molecular structures for evaluation. Thiazoles with an oxidized sulfur atom were not available for the present study. These molecular forms, however, are difficult to synthesize and would be expensive, according to R. A. Davis, UniRoyal Corporation (*personal communication*).

LITERATURE CITED

1. HALISKY, P. M., C. R. FUNK, & P. L. BABINSKI. 1968. Control of stripe smut in Kentucky bluegrass turf with a systemic fungicide. Plant Dis. Reptr. 52:635-637.
2. HARDISON, J. R. 1966. Chemotherapy of Urocystis agropyri in Merion Kentucky bluegrass (Poa pratensis L.) with two derivatives of 1,4-oxathiin. Crop Sci. 6:384.
3. HARDISON, J. R. 1967. Chemotherapeutic control of stripe smut (Ustilago striiformis) in grasses by two derivatives of 1,4-oxathiin. Phytopathology 57:242-245.
4. HARDISON, J. R. 1971. Relationships of molecular structure of 1,4-oxathiin fungicides to chemotherapeutic activity against rust and smut fungi in grasses. Phytopathology 61:731-735.
5. SNEL, M., B. VON SCHMELING, & L. V. EDGINGTON. 1970. Fungitoxicity and structure-activity relationships of some oxathiin and thiazole derivatives. Phytopathology 60:1164-1169.
6. WORF, G. L., & R. W. AHRENS. 1968. Bluegrass (Merion Kentucky) stripe smut (Ustilago striiformis). Fungicide and nematicide tests, results of 1968. Amer. Phytopathol. Soc. 24:90.